

Mass transport in a strongly sheared binary mixture of Maxwell molecules

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Transport coefficients associated with the mass flux of a binary mixture of Maxwell molecules under uniform shear flow are exactly determined from the Boltzmann kinetic equation. A normal solution is obtained via a Chapman–Enskog-like expansion around a local shear flow distribution that retains all the hydrodynamics orders in the shear rate. In the first order of the expansion the mass flux is proportional to the gradients of mole fraction, pressure, and temperature but, due to the anisotropy induced in the system by the shear flow, mutual diffusion, pressure diffusion and thermal diffusion tensors are identified instead of the conventional scalar coefficients. These tensors are obtained in terms of the shear rate and the parameters of the mixture (particle masses, concentrations, and force constants). The description is made both in the absence and in the presence of an external thermostat introduced in computer simulations to compensate for the viscous heating. As expected, the analysis shows that there is not a simple relationship between the results with and without the thermostat. The dependence of the three diffusion tensors on the shear rate is illustrated in the tracer limit case, the results showing that the deviation of the generalized transport coefficients from their equilibrium forms is in general quite important. Finally, the generalized transport coefficients associated with the momentum and heat transport are evaluated from a model kinetic equation of the Boltzmann equation.

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I. INTRODUCTION

The description of transport properties for states close to equilibrium in gaseous binary mixtures is well established. In these situations, the Curie principle¹ states that the presence of a velocity gradient (second-rank tensorial quantity) cannot modify a vectorial quantity such as the mass flux \mathbf{j}_1 , which is generated by gradients of mole fraction x_1 , pressure p , and temperature T . As a consequence, the mutual diffusion coefficient D (which couples the mass current with ∇x_1), the pressure diffusion coefficient D_p (which couples the mass current with ∇p) and the thermal diffusion coefficient D_T (which couples the mass current with ∇T) do not depend on the velocity gradient. However, when the shear rate applied is large, non-Newtonian effects are important so that the Curie principle does not hold and the coefficients associated with the mass transport are affected by the presence of shear flow. In particular, if the spatial gradients ∇x_1 , ∇p , and ∇T are weak, one expects that the flux \mathbf{j}_1 is still linear in these gradients but the standard scalar coefficients $\{D, D_p, D_T\}$ must be replaced by the shear-rate dependent second-rank tensors $\{D_{ij}, D_{p,ij}, D_{T,ij}\}$. The aim of this paper is to determine the above tensors in the framework of the Boltzmann equation.

We are interested in a situation where *weak* spatial gradients of mole fraction, pressure, and temperature coexist with a *strong* shear rate. Under these conditions, the application of the conventional Chapman–Enskog expansion² around the local equilibrium state to get higher order hydrodynamic effects (Burnett, super-Burnett, ...) to the mass flux turns out to be extremely difficult. This gives rise to look for alternative approaches. A possibility is to expand around a more relevant reference state than local equilibrium. Since we want to compute the mass transport in a strongly sheared mixture, the so-called uniform shear flow (USF) state can be chosen as the reference state. The USF state is characterized by constant mole fractions, a uniform temperature, and a linear velocity profile $u_x = ay$, where a is the constant shear rate. Due to its simplicity, this state has been widely used in the past to shed light on the complexities associated with the *nonlinear* response of the system to the action of strong shearing. In addition, the USF state is one of the rare exceptions for which the hierarchy of moments of the Boltzmann equation admits an exact solution for single³ and multicomponent gases⁴ of Maxwell molecules (repulsive potential of the form r^{-4}). In this case, explicit expressions of the pressure tensor (which is the relevant irreversible flux of the problem) have been obtained for *arbitrary* values of the shear rate and the parameters of the system (masses, concentrations and force constants).

As said before, here we want to compute the mass transport under USF for Maxwell molecules. Since the mixture is slightly perturbed from the USF, the Boltzmann equation can be solved by an expansion in small gradients around the (local) shear flow distribution instead of the (local) equilibrium. This is the main feature of the expansion since the reference state is not restricted to small values of the shear rate. In the first order of the expansion, the set of generalized transport coefficients $\{D_{ij}, D_{p,ij}, D_{T,ij}\}$ are identified from the mass flux \mathbf{j}_1 as nonlinear functions of the shear rate and the parameters of the mixture. This Chapman–Enskog-like expansion has been used to analyze transport properties in spatially inhomogeneous states near USF in the case of ordinary gases^{5,6} and more recently

in the context of granular gases.^{7,8,9}

Some previous attempts have been carried out earlier by the author and coworkers^{10,11,12,13,14} in the case of the diffusion tensor D_{ij} . However, all these studies have been restricted to perturbed *steady* states with the constraints $p = \text{const}$ and $T = \text{const}$. Although steady states are in general desirable for practical purposes, especially in computer simulations,¹⁵ here we extend the above studies to a general time and space dependence of the hydrodynamic fields. This allows us to evaluate new contributions to the mass flux (those proportional to ∇p and ∇T), which were not taken into account in the previous studies.⁶

The plan of the paper is as follows. First, a brief summary of the results obtained from the Boltzmann equation for a binary mixture of Maxwell molecules under USF is presented in Sec. II. Section III deals with the perturbation scheme used to solve the Boltzmann equation for the mixture to first order in the deviations of the hydrodynamic field gradients from their values in the reference shear flow state. The generalized transport coefficients characterizing the mass transport around USF are also defined in Sec. III. These coefficients are explicitly obtained in Sec. IV with and without the presence of an external thermostat introduced usually in computer simulations to compensate for the viscous heating. The dependence of some of these coefficients on the shear rate is illustrated with detail in the tracer limit case, showing that the influence of shear flow on mass transport is quite significant. The paper is closed by a brief discussion of the results in Sec. V, the generalized transport coefficients associated with the momentum and heat transport are evaluated in Appendix D from a simple model kinetic equation of the Boltzmann equation.

II. A BINARY MIXTURE UNDER UNIFORM SHEAR FLOW

We consider a *dilute* binary mixture where $f_s(\mathbf{r}, \mathbf{v}; t)$ is the one-particle velocity distribution function of species s ($s = 1, 2$). The time evolution of the distributions f_s is given by the set of two coupled nonlinear Boltzmann equations:

$$\left(\partial_t + \mathbf{v} \cdot \nabla + \frac{\partial}{\partial \mathbf{v}} \cdot \frac{\mathbf{F}_s}{m_s} \right) f_s(\mathbf{r}, \mathbf{v}, t) = \sum_{r=1}^2 J_{sr} [\mathbf{v} | f_s(t), f_r(t)] , \quad (2.1)$$

where m_s is the mass of a particle of species s , \mathbf{F}_s is a possible external force acting on particles of species s , and $J_{sr} [\mathbf{v} | f_s, f_r]$ is the Boltzmann collision operator, which in standard notation reads²

$$J_{sr} [f_s, f_r] = \int d\mathbf{v}_1 \int d\Omega |\mathbf{v} - \mathbf{v}_1| \sigma_{sr}(\mathbf{v} - \mathbf{v}_1, \theta) [f_s(\mathbf{v}') f_r(\mathbf{v}_1') - f_s(\mathbf{v}) f_r(\mathbf{v}_1)] . \quad (2.2)$$

The basic moments of f_s are the species number densities

$$n_s = \int d\mathbf{v} f_s, \quad (2.3)$$

and the mean velocity of species s

$$\mathbf{u}_s = \frac{1}{n_s} \int d\mathbf{v} \mathbf{v} f_s. \quad (2.4)$$

These quantities define the total number density $n = \sum_s n_s$ and the flow velocity $\mathbf{u} = \sum_s \rho_s \mathbf{u}_s / \rho$, where $\rho_s = m_s n_s$ is the mass density of species s and $\rho = \sum_s \rho_s$ is the total mass density. The temperature T is defined as

$$nk_B T = \sum_s n_s k_B T_s = \sum_s \frac{m_s}{3} \int d\mathbf{v} \mathbf{V}^2 f_s, \quad (2.5)$$

where k_B is the Boltzmann constant and $\mathbf{V} = \mathbf{v} - \mathbf{u}$ is the peculiar velocity. The second identity in (2.5) defines the partial kinetic temperatures T_s of species s . They measure the mean kinetic energy of particles of species s . Moreover, in a dilute gas the hydrostatic pressure p is given by $p = nk_B T$. The quantities n_s , \mathbf{u} , and T are associated with the densities of conserved quantities (mass of each species, total momentum, and total energy). The corresponding balance equations define the dissipative fluxes of mass

$$\mathbf{j}_s = m_s \int d\mathbf{v} \mathbf{V} f_s, \quad (2.6)$$

momentum (pressure tensor),

$$\mathbf{P} = \sum_s \mathbf{P}_s = \sum_s m_s \int d\mathbf{v} \mathbf{V} \mathbf{V} f_s, \quad (2.7)$$

and energy (heat flux)

$$\mathbf{q} = \sum_s \mathbf{q}_s = \sum_s \frac{m_s}{2} \int d\mathbf{v} \mathbf{V}^2 \mathbf{V} f_s. \quad (2.8)$$

The second equalities in Eqs. (2.7) and (2.8) define the partial contributions \mathbf{P}_s and \mathbf{q}_s to the pressure tensor and heat flux, respectively. The fact that the mass flux \mathbf{j}_s is defined with respect to the local center-of-mass velocity \mathbf{u} implies that

$$\sum_s \mathbf{j}_s = \mathbf{0}. \quad (2.9)$$

The USF state is macroscopically defined by constant densities n_s , a spatially uniform temperature $T(t)$ and a linear velocity profile $\mathbf{u}(y) = \mathbf{u}_1(y) = \mathbf{u}_2(y) = ay\hat{\mathbf{x}}$, where a is the *constant* shear rate. Since n_s and T are uniform, then $\mathbf{j}_s = \mathbf{q} = \mathbf{0}$, and the transport of momentum (measured by the pressure tensor) is the relevant phenomenon. In the USF problem, the temperature tends to increase in time due to viscous heating. Usually, an external force (thermostat) is introduced in computer simulations to remove this heating effect and keep the temperature constant.¹⁵ The simplest choice is a Gaussian isokinetic thermostat given by

$$\mathbf{F}_s = -m_s \alpha \mathbf{V}, \quad (2.10)$$

where the thermostat parameter α is a function of the shear rate adjusted as to keep the temperature constant. The implicit assumption behind the introduction of these forces is that they play a neutral role in the transport properties, so that the latter are the same with and without a thermostat, when conveniently scaled with the thermal speed. Nevertheless, this expectation is not in general true, except for some specific situations and/or interaction potentials.^{6,16}

At a microscopic level, the USF is characterized by a velocity distribution function that becomes *uniform* in the local Lagrangian frame, i.e., $f_s(\mathbf{r}, \mathbf{v}; t) = f_s(\mathbf{V}, t)$. In that case, Eq. (2.1) with the choice (2.10) reduces to

$$\frac{\partial}{\partial t} f_1 - \frac{\partial}{\partial V_i} (a_{ij} V_j + \alpha V_i) f_1 = J_{11}[f_1, f_1] + J_{12}[f_1, f_2] \quad (2.11)$$

and a similar equation for f_2 . Here, $a_{ij} = a\delta_{ix}\delta_{jy}$. The hierarchy of velocity moments associated with the Boltzmann equation (2.11) can be recursively solved in the particular case of Maxwell molecules, i.e., when particles of species r and s interact through a potential of the form $V_{rs}(r) = \kappa_{rs} r^{-4}$. The key point is that for this interaction the collision rate $g\sigma_{rs}(g, \theta)$ is independent of the relative velocity g and so the collisional moments of order k only involve moments of degree smaller than or equal to k . In particular, the first- and second-degree collisional moments are given by^{17,18}

$$m_s \int d\mathbf{v} \mathbf{V} J_{sr}[f_s, f_r] = -\frac{\lambda_{sr}}{m_s m_r} (\rho_s \mathbf{j}_r - \rho_r \mathbf{j}_s), \quad (2.12)$$

$$\begin{aligned} m_s \int d\mathbf{v} \mathbf{V} \mathbf{V} J_{sr}[f_s, f_r] &= \frac{\lambda'_{sr}}{(m_s + m_r) m_s} \left[\left(\rho_s p_r + \rho_r p_s - \frac{2}{3} \mathbf{j}_s \cdot \mathbf{j}_r \right) \mathbb{1} \right. \\ &\quad \left. - \rho_s \mathbf{P}_r - \rho_r \mathbf{P}_s + \mathbf{j}_s \mathbf{j}_r + \mathbf{j}_r \mathbf{j}_s \right] \\ &\quad - \frac{\lambda_{sr}}{(m_s + m_r) m_s} \left[2 \left(\frac{m_s}{m_r} \rho_r \mathbf{P}_s - \rho_s \mathbf{P}_r \right) \right. \\ &\quad \left. + \left(1 - \frac{m_s}{m_r} \right) (\mathbf{j}_s \mathbf{j}_r + \mathbf{j}_r \mathbf{j}_s) \right], \end{aligned} \quad (2.13)$$

where $p_s = \frac{1}{3} \text{tr} \mathbf{P}_s = n_s k_B T_s$ is the partial hydrostatic pressure and

$$\lambda_{sr} = 1.69\pi \left(\kappa_{sr} \frac{m_s m_r}{m_s + m_r} \right)^{1/2}, \quad \lambda'_{sr} = 2.61\pi \left(\kappa_{sr} \frac{m_s m_r}{m_s + m_r} \right)^{1/2}. \quad (2.14)$$

Thanks to the above property, exact expressions of the pressure tensor \mathbf{P} for a binary mixture of Maxwell molecules under USF were obtained some time ago.⁴ The nonzero elements of \mathbf{P} are related to the rheological properties of the mixture, namely, the nonlinear shear viscosity and the viscometric functions. In reduced units, they turn out to be nonlinear functions of the (reduced) shear rate $a^* = a/\zeta$ (where ζ is a convenient time unit defined below) and the parameters of the mixture: the mass ratio $\mu = m_1/m_2$, the mole fraction $x_1 = n_1/n$ and the force constant ratios κ_{11}/κ_{12} and κ_{22}/κ_{12} . It must be noted that in the particular case of Maxwell molecules there is an exact equivalence between the USF results with and without the external forces (2.10). As will be shown below, beyond the USF problem, the presence of the thermostat does not play a neutral role in the results and a certain influence may exist.

III. CHAPMAN-ENSKOG-LIKE EXPANSION AROUND USF

As said in the Introduction, the main aim of this work is to analyze mass transport of a dilute binary mixture subjected to USF. In that case, let us assume that the USF state is disturbed by small spatial perturbations. The response of the system to those perturbations gives rise to contributions to the mass flux that can be characterized by generalized transport coefficients. This Section is devoted to the evaluation of those coefficients.

In order to analyze this problem we have to start from the set of Boltzmann equations (2.1) with a general time and space dependence. Let $\mathbf{u}_0 = \mathbf{a} \cdot \mathbf{r}$ be the flow velocity of the *undisturbed* USF state, where the elements of the tensor \mathbf{a} are $a_{ij} = a\delta_{ix}\delta_{jy}$. In the *disturbed* state, however the true velocity \mathbf{u} is in general different from \mathbf{u}_0 , i.e., $\mathbf{u} = \mathbf{u}_0 + \delta\mathbf{u}$, $\delta\mathbf{u}$ being a small perturbation to \mathbf{u}_0 . As a consequence, the true peculiar velocity is now $\mathbf{c} \equiv \mathbf{v} - \mathbf{u} = \mathbf{V} - \delta\mathbf{u}$, where $\mathbf{V} = \mathbf{v} - \mathbf{u}_0$. In the Lagrangian frame moving with \mathbf{u}_0 , the Boltzmann equations (2.1) can be written as

$$\frac{\partial}{\partial t} f_1 - \frac{\partial}{\partial V_i} (a_{ij} V_j + \alpha V_i) f_1 + (\mathbf{V} + \mathbf{u}_0) \cdot \nabla f_1 + \alpha \delta\mathbf{u} \cdot \frac{\partial f_1}{\partial \mathbf{V}} = J_{11}[f_1, f_1] + J_{12}[f_1, f_2], \quad (3.1a)$$

$$\frac{\partial}{\partial t} f_2 - \frac{\partial}{\partial V_i} (a_{ij} V_j + \alpha V_i) f_2 + (\mathbf{V} + \mathbf{u}_0) \cdot \nabla f_2 + \alpha \delta\mathbf{u} \cdot \frac{\partial f_2}{\partial \mathbf{V}} = J_{22}[f_2, f_2] + J_{21}[f_2, f_1], \quad (3.1b)$$

where here the derivative ∇f_s is taken at constant \mathbf{V} . In addition, in Eqs. (3.1a) and (3.1b) the thermostat force has been assumed to be proportional to the actual peculiar velocity, $\mathbf{F}_s = -m_s \alpha (\mathbf{V} - \delta\mathbf{u})$ where now the parameter α is in general a function of \mathbf{r} and t through their functional dependence on the hydrodynamic fields n_s and T . The generalization of α to the inhomogeneous case is essentially a matter of choice. Here, for the sake of simplicity, we will take two different choices for α : (i) $\alpha = 0$, so that the temperature grows in time, and (ii) the same expression obtained in the (pure) USF problem, except that the densities and temperature are replaced by those of the general inhomogeneous state.

The macroscopic balance equations associated with this disturbed USF state are obtained by taking moments in Eqs. (3.1a) and (3.1b) with the result

$$\partial_t n_s + \mathbf{u}_0 \cdot \nabla n_s + \nabla \cdot (n_s \delta\mathbf{u}) = -\frac{\nabla \cdot \mathbf{j}_s}{m_s}, \quad (3.2)$$

$$\partial_t \delta u_i + a_{ij} \delta u_j + (\mathbf{u}_0 + \delta\mathbf{u}) \cdot \nabla \delta u_i = -\rho^{-1} \nabla_j P_{ij}, \quad (3.3)$$

$$\frac{3}{2} n \partial_t T + \frac{3}{2} n (\mathbf{u}_0 + \delta\mathbf{u}) \cdot \nabla T = -a P_{xy} + \frac{3}{2} T \sum_{s=1}^2 \frac{\nabla \cdot \mathbf{j}_s}{m_s} - (\nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \delta\mathbf{u} + 3p\alpha), \quad (3.4)$$

where the mass flux \mathbf{j}_s , the pressure tensor \mathbf{P} , and the heat flux \mathbf{q} are defined by Eqs. (2.6), (2.7), and (2.8), respectively, with the replacement $\mathbf{V} \rightarrow \mathbf{c}$. The corresponding balance equations for the mole fraction $x_1 = n_1/n$ and the pressure $p = nk_B T$ can be obtained from Eqs. (3.2) and (3.4). They are given by

$$\partial_t x_1 + (\mathbf{u}_0 + \delta\mathbf{u}) \cdot \nabla x_1 = -\frac{\rho}{n^2 m_1 m_2} \nabla \cdot \mathbf{j}_1, \quad (3.5)$$

$$\partial_t p + (\mathbf{u}_0 + \delta\mathbf{u}) \cdot \nabla p + p \nabla \cdot \delta\mathbf{u} = -\frac{2}{3} (a P_{xy} + \nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \delta\mathbf{u} + 3p\alpha). \quad (3.6)$$

We assume that the deviations from the USF state are small. This means that the spatial gradients of the hydrodynamic fields are small. For systems near equilibrium, the specific set of gradients contributing to each flux is restricted by fluid symmetry, Onsager relations, and the form of entropy production.¹ However, in far from equilibrium situations (such as the one considered in this paper), only fluid symmetry applies and so there is more flexibility in the representation of the heat and mass fluxes since they can be defined in a variety of equivalent ways depending on the choice of hydrodynamic gradients used. In fact, some care is required in comparing transport coefficients in different representations using different independent gradients for the driving forces. Here, as in previous works,^{9,19,20} the mole fraction x_1 , the pressure p , the temperature T , and the local flow velocity $\delta\mathbf{u}$ are chosen as hydrodynamic fields.

Since the system is strongly sheared, a solution to the set of Boltzmann equations (3.1a) and (3.1b) can be obtained by means of a generalization of the conventional Chapman-Enskog method² in which the velocity distribution function

is expanded around a *local* shear flow reference state in terms of the small spatial gradients of the hydrodynamic fields relative to those of USF. This is the main new ingredient of the expansion. This type of Chapman-Enskog-like expansion has been already considered to get the set of shear-rate dependent transport coefficients^{5,13,14} in thermostatted shear flow problems and it has also been recently used for inelastic gases.^{7,8,9}

In the context of the Chapman-Enskog method,² we look for a *normal* solution of the form

$$f_s(\mathbf{r}, \mathbf{V}, t) \equiv f_s[A(\mathbf{r}, t), \mathbf{V}], \quad (3.7)$$

where

$$A(\mathbf{r}, t) \equiv \{x_1(\mathbf{r}, t), p(\mathbf{r}, t), T(\mathbf{r}, t), \delta\mathbf{u}(\mathbf{r}, t)\}. \quad (3.8)$$

This special solution expresses the fact that the space dependence of the reference shear flow is completely absorbed in the relative velocity \mathbf{V} and all other space and time dependence occurs entirely through a *functional* dependence on the fields $A(\mathbf{r}, t)$. The functional dependence (3.4) can be made local by an expansion of the distribution function in powers of the hydrodynamic gradients:

$$f_s[A(\mathbf{r}, t), \mathbf{V}] = f_s^{(0)}(\mathbf{V}) + f_s^{(1)}(\mathbf{V}) + \dots, \quad (3.9)$$

where the reference zeroth-order distribution function corresponds to the USF distribution function but taking into account the local dependence of the concentration, pressure and temperature and the change $\mathbf{V} \rightarrow \mathbf{V} - \delta\mathbf{u}(\mathbf{r}, t) = \mathbf{c}$. The successive approximations $f_s^{(k)}$ are of order k in the gradients of x_1 , p , T , and $\delta\mathbf{u}$ but retain all the orders in the shear rate a . Here, only the first-order approximation will be analyzed.

When the expansion (3.9) is substituted into the definitions (2.6), (2.7), and (2.8), one gets the corresponding expansions for the fluxes:

$$\mathbf{j}_s = \mathbf{j}_s^{(0)} + \mathbf{j}_s^{(1)} + \dots, \quad (3.10a)$$

$$\mathbf{P} = \mathbf{P}^{(0)} + \mathbf{P}^{(1)} + \dots, \quad \mathbf{q} = \mathbf{q}^{(0)} + \mathbf{q}^{(1)} + \dots. \quad (3.10b)$$

Finally, as in the usual Chapman-Enskog method, the time derivative is also expanded as

$$\partial_t = \partial_t^{(0)} + \partial_t^{(1)} + \partial_t^{(2)} + \dots, \quad (3.11)$$

where the action of each operator $\partial_t^{(k)}$ is obtained from the hydrodynamic equations (3.2)–(3.4). These results provide the basis for generating the Chapman-Enskog solution to the Boltzmann equations (3.1a) and (3.1b).

A. Zeroth-order approximation

Substituting the expansions (3.10a)–(3.11) into Eq. (3.1a), the kinetic equation for $f_1^{(0)}$ is given by

$$\frac{\partial}{\partial t} f_1^{(0)} - \frac{\partial}{\partial V_i} (a_{ij} V_j + \alpha V_i) f_1^{(0)} + (\mathbf{V} + \mathbf{u}_0) \cdot \nabla f_1^{(0)} + \alpha \delta\mathbf{u} \cdot \frac{\partial f_1^{(0)}}{\partial \mathbf{V}} = J_{11}[f_1^{(0)}, f_1^{(0)}] + J_{12}[f_1^{(0)}, f_2^{(0)}]. \quad (3.12)$$

To lowest order in the expansion the conservation laws give

$$\partial_t^{(0)} x_1 = 0, \quad T^{-1} \partial_t^{(0)} T = p^{-1} \partial_t^{(0)} p = -\frac{2}{3p} a P_{xy}^{(0)} - 2\alpha, \quad (3.13)$$

$$\partial_t^{(0)} \delta u_i + a_{ij} \delta u_j = 0. \quad (3.14)$$

If $\alpha = 0$, then $T^{-1} \partial_t^{(0)} T = p^{-1} \partial_t^{(0)} p = -2a P_{xy}^{(0)} / 3p$ while if $\alpha = -a P_{xy}^{(0)} / 3p$ then $\partial_t^{(0)} T = \partial_t^{(0)} p = 0$.

Since $f_1^{(0)}$ is a normal solution, the time derivative in Eq. (3.12) can be represented more usefully as

$$\begin{aligned} \partial_t^{(0)} f_1^{(0)} &= \frac{\partial f_1^{(0)}}{\partial x_1} \partial_t^{(0)} x_1 + \frac{\partial f_1^{(0)}}{\partial p} \partial_t^{(0)} p + \frac{\partial f_1^{(0)}}{\partial T} \partial_t^{(0)} T + \frac{\partial f_1^{(0)}}{\partial \delta u_i} \partial_t^{(0)} \delta u_i \\ &= -\left(\frac{2}{3p} a P_{xy}^{(0)} + 2\alpha\right) \left(p \frac{\partial}{\partial p} + T \frac{\partial}{\partial T}\right) f_1^{(0)} - a_{ij} \delta u_j \frac{\partial}{\partial \delta u_i} f_1^{(0)} \\ &= -\left(\frac{2}{3p} a P_{xy}^{(0)} + 2\alpha\right) \left(p \frac{\partial}{\partial p} + T \frac{\partial}{\partial T}\right) f_1^{(0)} + a_{ij} \delta u_j \frac{\partial}{\partial c_i} f_1^{(0)}, \end{aligned} \quad (3.15)$$

where in the last step we have taken into account that $f_1^{(0)}$ depends on $\delta \mathbf{u}$ only through the peculiar velocity \mathbf{c} . Substituting Eq. (3.15) into Eq. (3.12) yields the following kinetic equation for $f_1^{(0)}$:

$$\begin{aligned} & - \left(\frac{2}{3p} a P_{xy}^{(0)} + 2\alpha \right) \left(p \frac{\partial}{\partial p} + T \frac{\partial}{\partial T} \right) f_1^{(0)} - a c_y \frac{\partial}{\partial c_x} f_1^{(0)} - \alpha \frac{\partial}{\partial \mathbf{c}} \cdot (\mathbf{c} f_1^{(0)}) \\ & = J_{11}[f_1^{(0)}, f_1^{(0)}] + J_{12}[f_1^{(0)}, f_2^{(0)}]. \end{aligned} \quad (3.16)$$

A similar equation holds for $f_2^{(0)}$. The partial pressure tensors $\mathbf{P}_1^{(0)}$ and $\mathbf{P}_2^{(0)}$ can be obtained from Eq. (3.16) and its counterpart for $f_2^{(0)}$ when one multiplies both equations by $m_s \mathbf{c} \mathbf{c}$ and integrate over \mathbf{c} . Their explicit forms can be found in the Appendix of Ref. 4.

B. First-order approximation

The analysis to first order in the gradients is worked out in Appendix A. The distribution function $f_1^{(1)}$ is of the form

$$f_1^{(1)} = \mathbf{A}_1 \cdot \nabla x_1 + \mathbf{B}_1 \cdot \nabla p + \mathbf{C}_1 \cdot \nabla T + \mathcal{D}_1 : \nabla \delta \mathbf{u}, \quad (3.17)$$

where the vectors $\{\mathbf{A}_1, \mathbf{B}_1, \mathbf{C}_1\}$, and the tensor \mathcal{D}_1 are functions of the true peculiar velocity \mathbf{c} . They are the solutions of the following set of linear integral equations:

$$\begin{aligned} & - \left(\frac{2}{3p} a P_{xy}^{(0)} + 2\alpha \right) (p \partial_p + T \partial_T) \mathbf{A}_1 - \left(a c_y \frac{\partial}{\partial c_x} + \alpha \frac{\partial}{\partial \mathbf{c}} \cdot \mathbf{c} \right) \mathbf{A}_1 + \mathcal{L}_1 \mathbf{A}_1 + \mathcal{M}_1 \mathbf{A}_2 \\ & = \mathbf{A}_1 + \left(\frac{2a}{3p} \partial_{x_1} P_{xy}^{(0)} + 2\partial_{x_1} \alpha \right) (p \mathbf{B}_1 + T \mathbf{C}_1), \end{aligned} \quad (3.18)$$

$$\begin{aligned} & - \left(\frac{2}{3p} a P_{xy}^{(0)} + 2\alpha \right) (p \partial_p + T \partial_T) \mathbf{B}_1 - \left(a c_y \frac{\partial}{\partial c_x} + \alpha \frac{\partial}{\partial \mathbf{c}} \cdot \mathbf{c} \right) \mathbf{B}_1 + \mathcal{L}_1 \mathbf{B}_1 + \mathcal{M}_1 \mathbf{B}_2 \\ & - \left[\frac{2a}{3} \partial_p P_{xy}^{(0)} + 2(1 + p \partial_p) \alpha \right] \mathbf{B}_1 = \mathbf{B}_1 - \left[\frac{2aT}{3p^2} (1 - p \partial_p) P_{xy}^{(0)} - 2T \partial_p \alpha \right] \mathbf{C}_1, \end{aligned} \quad (3.19)$$

$$\begin{aligned} & - \left(\frac{2}{3p} a P_{xy}^{(0)} + 2\alpha \right) (p \partial_p + T \partial_T) \mathbf{C}_1 - \left(a c_y \frac{\partial}{\partial c_x} + \alpha \frac{\partial}{\partial \mathbf{c}} \cdot \mathbf{c} \right) \mathbf{C}_1 + \mathcal{L}_1 \mathbf{C}_1 + \mathcal{M}_1 \mathbf{C}_2 \\ & - \left[\frac{2a}{3p} (1 + T \partial_T) P_{xy}^{(0)} + 2(1 + T \partial_T) \alpha \right] \mathbf{C}_1 = \mathbf{C}_1 + \left(\frac{2a}{3} \partial_T P_{xy}^{(0)} + 2p \partial_T \alpha \right) \mathbf{B}_1, \end{aligned} \quad (3.20)$$

$$\begin{aligned} & - \left(\frac{2}{3p} a P_{xy}^{(0)} + 2\alpha \right) (p \partial_p + T \partial_T) \mathcal{D}_{1,\ell j} - \left(a c_y \frac{\partial}{\partial c_x} + \alpha \frac{\partial}{\partial \mathbf{c}} \cdot \mathbf{c} \right) \mathcal{D}_{1,\ell j} - a \delta_{\ell y} \mathcal{D}_{1,xj} \\ & + \mathcal{L}_1 \mathcal{D}_{1,\ell j} + \mathcal{M}_1 \mathcal{D}_{2,\ell j} = \mathcal{D}_{1,\ell j}, \end{aligned} \quad (3.21)$$

where $\mathbf{A}_1(\mathbf{c})$, $\mathbf{B}_1(\mathbf{c})$, $\mathbf{C}_1(\mathbf{c})$, and $\mathcal{D}_1(\mathbf{c})$ are defined by Eqs. (A8)–(A11), respectively. In addition, \mathcal{L}_1 and \mathcal{M}_1 are the linearized Boltzmann collision operators around the reference USF state:

$$\mathcal{L}_1 X = - \left(J_{11}[f_1^{(0)}, X] + J_{11}[X, f_1^{(0)}] + J_{12}[X, f_2^{(0)}] \right), \quad (3.22a)$$

$$\mathcal{M}_1 X = -J_{12}[f_2^{(0)}, X]. \quad (3.22b)$$

In this paper we are mainly interested in evaluating the first-order contribution to the mass flux $\mathbf{j}_1^{(1)}$. It is defined as

$$\mathbf{j}_1^{(1)} = m_1 \int d\mathbf{c} \mathbf{c} f_1^{(1)}, \quad \mathbf{j}_2^{(1)} = -\mathbf{j}_1^{(1)}. \quad (3.23)$$

Use of Eq. (3.17) into Eq. (3.23) gives the expression

$$j_{1,i}^{(1)} = -\frac{m_1 m_2 n}{\rho} D_{ij} \frac{\partial x_1}{\partial r_j} - \frac{\rho}{p} D_{p,ij} \frac{\partial p}{\partial r_j} - \frac{\rho}{T} D_{T,ij} \frac{\partial T}{\partial r_j}, \quad (3.24)$$

where

$$D_{ij} = -\frac{\rho}{m_2 n} \int d\mathbf{c} c_i \mathcal{A}_{1,j}(\mathbf{c}), \quad (3.25)$$

$$D_{p,ij} = -\frac{m_1 p}{\rho} \int d\mathbf{c} c_i \mathcal{B}_{1,j}(\mathbf{c}), \quad (3.26)$$

$$D_{T,ij} = -\frac{m_1 T}{\rho} \int d\mathbf{c} c_i \mathcal{C}_{1,j}(\mathbf{c}). \quad (3.27)$$

Upon writing Eqs. (3.25)–(3.27) use has been made of the symmetry properties of \mathcal{A}_1 , \mathcal{B}_1 , and \mathcal{C}_1 . In general, the set of *generalized* transport coefficients D_{ij} , $D_{p,ij}$, and $D_{T,ij}$ are nonlinear functions of the shear rate and the parameters of the mixture. It is apparent that the anisotropy induced by the presence of shear flow gives rise to new transport coefficients for the mass flux, reflecting broken symmetry. According to Eq. (3.24), the mass flux is expressed in terms of a diffusion tensor D_{ij} , a pressure diffusion tensor $D_{p,ij}$, and a thermal diffusion tensor $D_{T,ij}$.

To get the explicit dependence of the above transport coefficients on the parameter space of the problem, the form of α must be chosen. As said before, two choices will be considered here: (i) the unthermostatted case $\alpha = 0$, and (ii) the thermostatted case $\alpha = -aP_{xy}^{(0)}/3p$. Both cases will be separately studied in the next Section.

IV. MASS TRANSPORT UNDER SHEAR FLOW

This Section is devoted to the determination of the generalized transport coefficients D_{ij} , $D_{p,ij}$, and $D_{T,ij}$ associated with the mass transport for the two choices of the thermostat parameter. These coefficients are given in terms of the solutions to the integral equations (3.18)–(3.20).

A. Unthermostatted USF state

In the absence of an external thermostat ($\alpha = 0$), the integral equations (3.18)–(3.20) become

$$\begin{aligned} & -\frac{2}{3p} a P_{xy}^{(0)} (p \partial_p + T \partial_T) \mathcal{A}_1 - a c_y \frac{\partial}{\partial c_x} \mathcal{A}_1 + \mathcal{L}_1 \mathcal{A}_1 + \mathcal{M}_1 \mathcal{A}_2 \\ & = \mathbf{A}_1 + \frac{2a}{3p} (p \mathcal{B}_1 + T \mathcal{C}_1) (\partial_{x_1} P_{xy}^{(0)}), \end{aligned} \quad (4.1)$$

$$\begin{aligned} & -\frac{2}{3p} a P_{xy}^{(0)} (p \partial_p + T \partial_T) \mathcal{B}_1 - \left(\frac{2a}{3} \partial_p P_{xy}^{(0)} + a c_y \frac{\partial}{\partial c_x} \right) \mathcal{B}_1 + \mathcal{L}_1 \mathcal{B}_1 + \mathcal{M}_1 \mathcal{B}_2 \\ & = \mathbf{B}_1 - \frac{2aT}{3p^2} \mathcal{C}_1 (1 - p \partial_p) P_{xy}^{(0)}, \end{aligned} \quad (4.2)$$

$$\begin{aligned} & -\frac{2}{3p} a P_{xy}^{(0)} (p \partial_p + T \partial_T) \mathcal{C}_1 - \left[\frac{2a}{3p} (1 + T \partial_T) P_{xy}^{(0)} + a c_y \frac{\partial}{\partial c_x} \right] \mathcal{C}_1 + \mathcal{L}_1 \mathcal{C}_1 + \mathcal{M}_1 \mathcal{C}_2 \\ & = \mathbf{C}_1 + \frac{2a}{3} \mathcal{B}_1 (\partial_T P_{xy}^{(0)}). \end{aligned} \quad (4.3)$$

The dependence of $P_{ij}^{(0)}$ on the pressure p and temperature T occurs explicitly and through its dependence on the reduced shear rate $a^* = a/\zeta$. Here, the effective collision frequency ζ is given by⁴

$$\zeta = 2n \frac{\lambda'_{12}}{m_1 + m_2} = 2 \frac{p}{k_B T} \frac{\lambda'_{12}}{m_1 + m_2}, \quad (4.4)$$

where λ'_{12} is defined in Eq. (2.14). Consequently,

$$\partial_p P_{ij}^{(0)} = \partial_p p P_{ij}^*(a^*) = \left(1 - a^* \frac{\partial}{\partial a^*}\right) P_{ij}^*(a^*), \quad (4.5)$$

$$\partial_T P_{ij}^{(0)} = \partial_T p P_{ij}^*(a^*) = \frac{p}{T} a^* \frac{\partial}{\partial a^*} P_{ij}^*(a^*), \quad (4.6)$$

where $P_{ij}^* = P_{ij}^{(0)}/p$. In addition, the dependence of $P_{ij}^{(0)}$ on the mole fraction x_1 is also rather intricate and so the derivatives with respect to x_1 must be carried out with care.¹³ The generalized coefficients D_{ij} , $D_{p,ij}$, and $D_{T,ij}$ can be obtained from Eqs. (4.1)–(4.3) when one multiplies those equations by $m_1 c_i$ and integrates over \mathbf{c} . After some algebra (some technical details are provided in Appendix B), one arrives at the following set of coupled algebraic equations:

$$\left[\left(\frac{\rho \lambda_{12}}{m_1 m_2} - \frac{2}{3} a P_{xy}^* \right) \delta_{ik} + a_{ik} \right] D_{kj} = \frac{\rho k_B T}{m_1 m_2} \left(\partial_{x_1} P_{1,ij}^* - \frac{\rho_1}{\rho} \partial_{x_1} P_{ij}^* \right) + \frac{2a\rho^2}{3m_1 m_2 n} (\partial_{x_1} P_{xy}^*) (D_{p,ij} + D_{T,ij}), \quad (4.7)$$

$$\left[\left(\frac{\rho \lambda_{12}}{m_1 m_2} - \frac{2a}{3p} (1 - a^* \partial_{a^*}) P_{xy}^* \right) \delta_{ik} + a_{ik} \right] D_{p,kj} = \frac{p}{\rho} (1 - a^* \partial_{a^*}) \left(P_{1,ij}^* - \frac{\rho_1}{\rho} P_{ij}^* \right) - \frac{2a}{3} a^* D_{T,ij} (\partial_{a^*} P_{xy}^*), \quad (4.8)$$

$$\left[\left(\frac{\rho \lambda_{12}}{m_1 m_2} - \frac{2a}{3} (1 + a^* \partial_{a^*}) P_{xy}^* \right) \delta_{ik} + a_{ik} \right] D_{T,kj} = \frac{p}{\rho} a^* \partial_{a^*} \left(P_{1,ij}^* - \frac{\rho_1}{\rho} P_{ij}^* \right) + \frac{2a}{3} a^* D_{p,ij} (\partial_{a^*} P_{xy}^*), \quad (4.9)$$

where $P_s^* = P_s^{(0)}/p$ and use has been made of the relations (4.5) and (4.6).

In the absence of shear field ($a = 0$), then $P_{s,ij}^* = x_s \delta_{ij}$, and $P_{ij}^* = \delta_{ij}$, so that Eqs. (4.7)–(4.9) have the solutions $D_{ij} = D_0 \delta_{ij}$, $D_{p,ij} = D_{p,0} \delta_{ij}$, and $D_{T,ij} = 0$, where D_0 and $D_{p,0}$ are the conventional Navier-Stokes transport coefficients for Maxwell molecules.² Their expressions are

$$D_0 = \frac{k_B T}{\lambda_{12}}, \quad D_{p,0} = \frac{\rho_1 \rho_2}{\rho^3} (m_2 - m_1) D_0. \quad (4.10)$$

In this case the mass flux $\mathbf{j}^{(1)}$ can be written as^{1,2}

$$\mathbf{j}_1^{(1)} = - \frac{m_1 m_2 \rho_1 \rho_2}{k_B \rho^2} D_0 \frac{(\nabla \phi_1)_T - (\nabla \phi_2)_T}{T}, \quad (4.11)$$

where

$$\left(\frac{\nabla \phi_s}{T} \right)_T = \frac{1}{m_s} \nabla \ln(x_s p), \quad (4.12)$$

ϕ_s being the chemical potential per unit mass. The fact that the thermal diffusion coefficient vanishes when $a^* = 0$ is due to the interaction potential considered (Maxwell molecules) since this coefficient is different from zero for more general interaction potentials.² However, when the mixture is strongly sheared, the Boltzmann equation leads to contributions to the mass flux proportional to the thermal gradient, even for Maxwell molecules.

In the case of mechanically equivalent particles ($\mu = 1$, $\kappa_{11} = \kappa_{22} = \kappa_{12}$), $P_{1,ij}^* = x_1 P_{ij}^*$, $\partial_{x_1} P_{1,ij}^{(0)} = P_{1,ij}^{(0)}/x_1 = P_{xy}^{(0)}$, and so $D_{p,ij} = D_{T,ij} = 0$. Moreover, Eq. (4.7) reduces to

$$D_{ij} = \frac{m^{-1}}{n \lambda_{12}/m - \frac{2}{3} a P_{xy}^*} \left(\delta_{ik} - \frac{a_{ik}}{n \lambda_{12}/m - \frac{2}{3} a P_{xy}^*} \right) P_{kj}^{(0)}. \quad (4.13)$$

Equation (4.13) is consistent with previous results derived for the self-diffusion tensor.^{22,23} Furthermore, known results for the diffusion tensor¹⁰ are also recovered in the tracer limit ($x_1 \rightarrow 0$).

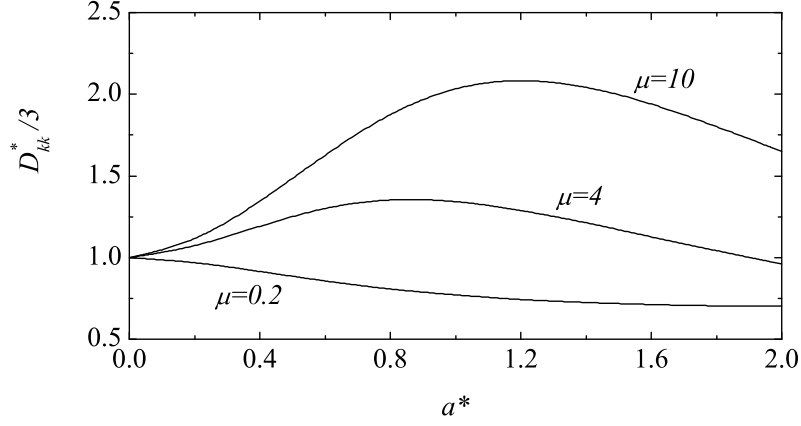


FIG. 1: Shear-rate dependence of the trace $\frac{1}{3}D_{kk}^*$ of the mutual diffusion tensor for $x_1 = 0$, $\kappa_{22} = \kappa_{12}$ and several values of the mass ratio $\mu = m_1/m_2$.

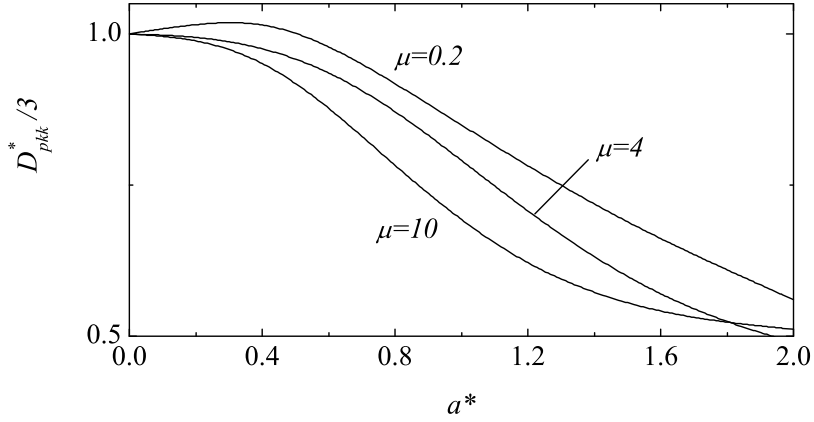


FIG. 2: Shear-rate dependence of the trace $\frac{1}{3}D_{p,kk}^*$ of the pressure diffusion tensor for $x_1 = 0$, $\kappa_{22} = \kappa_{12}$ and several values of the mass ratio $\mu = m_1/m_2$.

B. Thermostatted USF state

Let us assume now that an external thermostat is introduced to compensate for the viscous heating effect. In this case, $\alpha = -aP_{xy}^{(0)}/3p$, and the integral equations (3.18)–(3.20) become

$$-\left(ac_y \frac{\partial}{\partial c_x} + \alpha \frac{\partial}{\partial \mathbf{c}} \cdot \mathbf{c}\right) \mathcal{A}_1 + \mathcal{L}_1 \mathcal{A}_1 + \mathcal{M}_1 \mathcal{A}_2 = \mathbf{A}_1, \quad (4.14)$$

$$-\left(ac_y \frac{\partial}{\partial c_x} + \alpha \frac{\partial}{\partial \mathbf{c}} \cdot \mathbf{c}\right) \mathcal{B}_1 + \mathcal{L}_1 \mathcal{B}_1 + \mathcal{M}_1 \mathcal{B}_2 = \mathbf{B}_1, \quad (4.15)$$

$$-\left(ac_y \frac{\partial}{\partial c_x} + \alpha \frac{\partial}{\partial \mathbf{c}} \cdot \mathbf{c}\right) \mathcal{C}_1 + \mathcal{L}_1 \mathcal{C}_1 + \mathcal{M}_1 \mathcal{C}_2 = \mathbf{C}_1. \quad (4.16)$$

In contrast to what happens in the unthermostatted case, the different integral equations are now decoupled and hence the generalized coefficients of the mass transport can be obtained more easily. The mathematical steps to get them are similar to those made before when $\alpha = 0$ and so only the final results are presented. The explicit expressions for D_{ij} , $D_{p,ij}$, and $D_{T,ij}$ are given by

$$D_{ij} = \frac{\rho k_B T}{m_1 m_2} \frac{1}{\alpha + \frac{\rho \lambda_{12}}{m_1 m_2}} \left(\delta_{ik} - \frac{a_{ik}}{\alpha + \frac{\rho \lambda_{12}}{m_1 m_2}} \right) \left(\partial_{x_1} P_{1,kj}^* - \frac{\rho_1}{\rho} \partial_{x_1} P_{kj}^* \right), \quad (4.17)$$

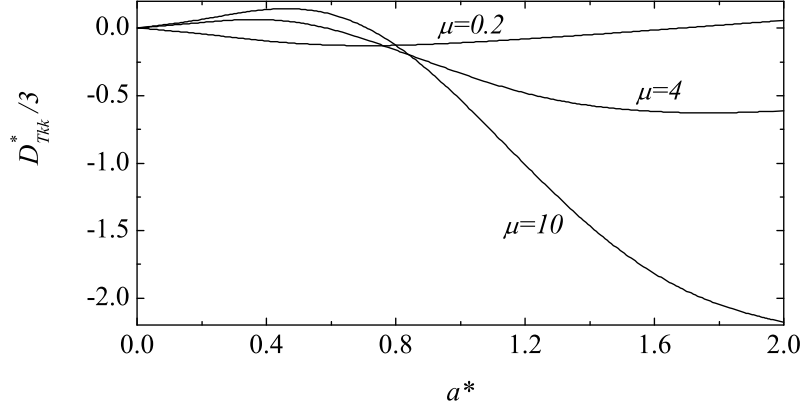


FIG. 3: Shear-rate dependence of the trace $\frac{1}{3}D_{T,kk}^*$ of the thermal diffusion tensor for $x_1 = 0$, $\kappa_{22} = \kappa_{12}$ and several values of the mass ratio $\mu = m_1/m_2$.

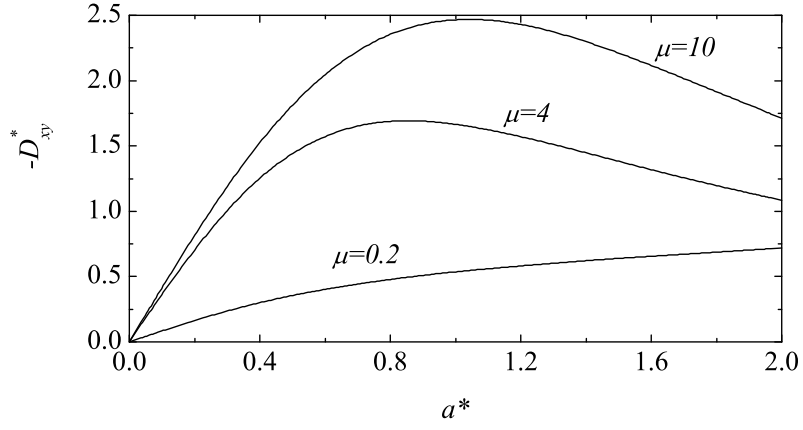


FIG. 4: Shear-rate dependence of the off-diagonal element $-D_{xy}^*$ of the mutual diffusion tensor for $x_1 = 0$, $\kappa_{22} = \kappa_{12}$ and several values of the mass ratio $\mu = m_1/m_2$.

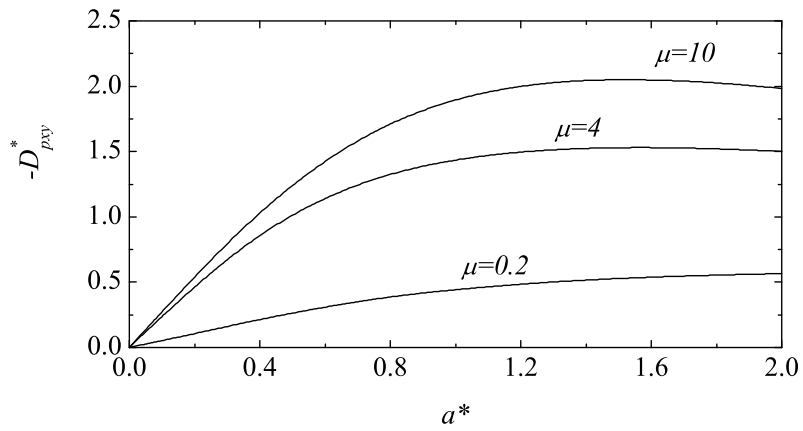


FIG. 5: Shear-rate dependence of the off-diagonal element $-D_{p,xy}^*$ of the pressure diffusion tensor for $x_1 = 0$, $\kappa_{22} = \kappa_{12}$ and several values of the mass ratio $\mu = m_1/m_2$.

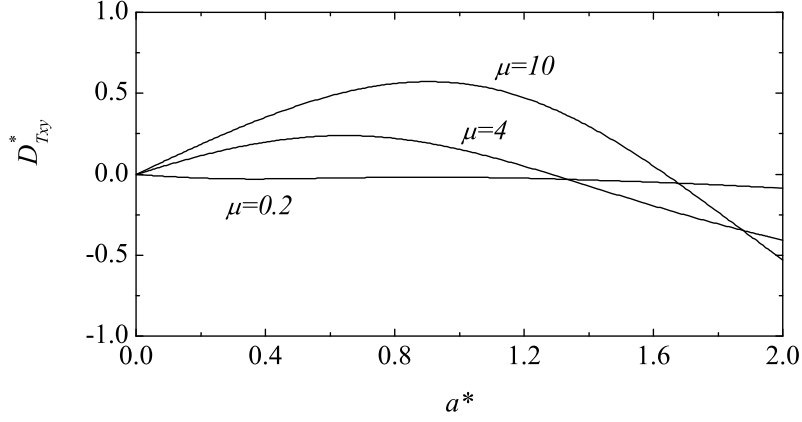


FIG. 6: Shear-rate dependence of the off-diagonal element $D_{T,xy}^*$ of the thermal diffusion tensor for $x_1 = 0$, $\kappa_{22} = \kappa_{12}$ and several values of the mass ratio $\mu = m_1/m_2$.

$$D_{p,ij} = \frac{p}{\rho} \frac{1}{\alpha + \frac{\rho\lambda_{12}}{m_1m_2}} \left(\delta_{ik} - \frac{a_{ik}}{\alpha + \frac{\rho\lambda_{12}}{m_1m_2}} \right) (1 - a^* \partial_{a^*}) \left(P_{1,kj}^* - \frac{\rho_1}{\rho} P_{kj}^* \right), \quad (4.18)$$

$$D_{T,ij} = \frac{p}{\rho} \frac{a^*}{\alpha + \frac{\rho\lambda_{12}}{m_1m_2}} \left(\delta_{ik} - \frac{a_{ik}}{\alpha + \frac{\rho\lambda_{12}}{m_1m_2}} \right) \partial_{a^*} \left(P_{1,kj}^* - \frac{\rho_1}{\rho} P_{kj}^* \right). \quad (4.19)$$

In order to get these expressions use has been made of the identity

$$(b\mathbb{1} + \mathbf{a})^{-1} = b^{-1}\mathbb{1} - b^{-2}\mathbf{a}, \quad (4.20)$$

where b is an arbitrary constant and \mathbf{a} is the tensor with elements $a_{ij} = a\delta_{ix}\delta_{jy}$.

In the case of mechanically equivalent particles, $D_{p,ij} = D_{T,ij} = 0$ and Eq. (4.17) reduces to

$$D_{ij} = \frac{m^{-1}}{\alpha + n\lambda_{12}/m} \left(\delta_{ik} - \frac{a_{ik}}{\alpha + n\lambda_{12}/m} \right) P_{kj}^{(0)}. \quad (4.21)$$

Equation (4.21) gives the self-diffusion tensor of tagged particles under thermostatted USF.²³ For a general binary mixture, the expression (4.17) for the diffusion tensor D_{ij} coincides with the one derived before¹³ in a stationary state with the constraints $p = \text{const}$ and $T = \text{const}$. Finally, it is also apparent that, except for vanishing shear rates, the expressions of the generalized transport coefficients (4.17)–(4.19) in the thermostatted state differ from the ones derived in the absence of a thermostat, Eqs. (4.7)–(4.9). This shows again that the presence of the thermostat affects the transport properties of the system.

V. ILLUSTRATIVE EXAMPLES IN THE TRACER LIMIT

The results obtained in the preceding Section give all the relevant information on the influence of shear flow on the mass transport. In general, the elements D_{ij} , $D_{p,ij}$ and $D_{T,ij}$ present a complex dependence on the shear rate and the parameters of the mixture without any restriction on their values. However, although the solution to Eqs. (4.7)–(4.9) (in the unthermostatted case) and Eqs. (4.17)–(4.19) (in the thermostatted case) is simple, it involves quite a tedious algebra due to the complex dependence of the partial pressure tensors $\mathbf{P}_{s,ij}^{(0)}$ and the thermostat parameter α on the mole fraction x_1 and the reduced shear rate a^* . To show the shear-rate dependence of the tensors $T_{ij} \equiv \{D_{ij}, D_{p,ij}, D_{T,ij}\}$ in a clearer way, the tracer limit ($x_1 \rightarrow 0$) will be considered here in detail. In addition, to make some contact with computer simulation results, the thermostatted case will be studied. In the tracer limit case, $\mathbf{P} \simeq \mathbf{P}_2$ and the partial pressure tensors \mathbf{P}_1 and \mathbf{P}_2 have a more simplified forms.¹⁰ In particular, $\partial_{x_1} P_{ij}^{(0)} = 0$ and $\partial_{x_1} P_{1,ij}^{(0)} = P_{1,ij}^{(0)}/x_1$. The explicit expressions of the partial pressure tensors in the tracer limit are provided in Appendix C.

As expected, $T_{xz} = T_{zx} = T_{yz} = T_{zy} = 0$, in agreement with the symmetry of the problem. As a consequence, there are five relevant elements: the three diagonal (T_{xx} , T_{yy} , and T_{zz}) and two off-diagonal elements (T_{xy} and T_{yx}). In addition, $T_{xx} \neq T_{yy} = T_{zz}$ and $T_{xy} \neq T_{yx}$. The equality $P_{s,yy} = P_{s,zz}$ implies $T_{yy} = T_{zz}$. This property is a consequence of the interaction model considered since for non-Maxwell molecules computer simulations show that the yy and zz elements of the pressure tensor are different.²¹ In Figs. 1–6, the relevant elements of tensors D_{ij}^* , $D_{p,ij}^*$ and $D_{T,ij}^*$ are plotted as functions of the reduced shear rate a^* for $\kappa_{12} = \kappa_{22}$ and several values of the mass ratio μ . Here, the tensors have been reduced with respect to their Navier-Stokes values (except $D_{T,ij}$), namely, $D_{ij}^* = D_{ij}/D_0$, $D_{p,ij}^* = D_{p,ij}/D_{p,0}$ and $D_{T,ij}^* = D_{T,ij}/x_1 D_0$. One third of the trace of these tensors is plotted in Figs. 1–3, while the xy element is plotted in Figs. 4–6. We observe that in general the influence of shear flow on the mass transport is quite important. It is also apparent that the anisotropy of the system, as measured by the traces $\frac{1}{3}D_{kk}^*$, $\frac{1}{3}D_{p,kk}^*$, and $\frac{1}{3}D_{T,kk}^*$, grows with the shear rate. This anisotropy is more significant when the impurity is heavier than the particles of the gas. Moreover, the shear field induces cross effects in the diffusion of particles. This is measured by the (reduced) off-diagonal elements D_{xy}^* , $D_{p,xy}^*$ and $D_{T,xy}^*$. These coefficients give the transport of mass along the x axis due to gradients parallel to the y axis. While D_{xy}^* and $D_{p,xy}^*$ are negative, the coefficient $D_{T,xy}$ can be positive in the region of small shear rates. We observe that, regardless of the mass ratio, the shapes of D_{xy}^* and $D_{p,xy}^*$ are quite similar: there is a region of values of a^* for which $-D_{xy}^*$ and $-D_{p,xy}^*$ increase with increasing shear rate, while the opposite happens for larger shear rates. The magnitude of $D_{T,xy}^*$ is smaller than that of the elements $-D_{xy}^*$ and $-D_{p,xy}^*$, especially when the tracer particles are lighter than the particles of the gas. In this latter case, $D_{T,xy}^*$ is practically negligible.

VI. DISCUSSION

Diffusion of particles in a binary mixture in non-Newtonian regimes is a subject of great interest from a fundamental and practical points of view. If the mixture is strongly sheared, the mass flux \mathbf{j}_1 can be significantly affected by the presence of shear flow so that the corresponding transport coefficients may differ significantly from their equilibrium values. In addition, the resulting mass transport is anisotropic and thus it cannot be described by scalar transport coefficients but by shear-rate dependent tensorial quantities whose explicit determination has been the main objective of this paper.

In order to gain some insight into this complex problem, a dilute binary mixture of Maxwell molecules under USF has been considered. This is perhaps the only interaction potential for which the Boltzmann equation can be exactly solved in some specific non-homogenous situations, such as in the case of the USF problem. In particular, the corresponding rheological properties of the mixture (nonlinear shear viscosity and viscometric functions) have been obtained for *arbitrary* values of the shear rate and without any restriction on the parameters of the mixture (masses, concentrations, and force constants).⁴ This exact solution is of great significance in providing insight into the type of phenomena that can occur in conditions far away from equilibrium. In this paper, the interest has been focused on situations that slightly deviate from the USF by small spatial gradients. Under these conditions, a generalized Chapman-Enskog method^{5,7,8,9} around the shear flow distribution has been used to determine mass transport in the first order of the deviations of the hydrodynamic field gradients from their values in the reference shear flow state $f_s^{(0)}$. In this case, the mass flux $\mathbf{j}_1^{(1)}$ is given by Eq. (3.24), where the corresponding set of generalized transport coefficients $\{D_{ij}, D_{p,ij}, D_{T,ij}\}$ are the solutions of the coupled algebraic equations (4.7)–(4.9) in the unthermostatted case, while they are explicitly given by Eqs. (4.17)–(4.19) in the presence of a Gaussian thermostat.¹⁵ This type of external forces are usually employed in nonequilibrium molecular dynamics simulations to compensate exactly for the viscous increase of temperature.

As expected, the results show that the coefficients $\{D_{ij}, D_{p,ij}, D_{T,ij}\}$ present a complex dependence on the shear rate and on the masses, mole fractions, and force constants. This is clearly illustrated in Figs. 1–6 for the tracer limit case ($x_1 \rightarrow 0$). The deviations of $\{D_{ij}, D_{p,ij}, D_{T,ij}\}$ from their equilibrium values are basically due to three different reasons. First, the presence of shear flow modifies the collision frequency of the conventional diffusion problem ($\rho\lambda_{12}/m_1m_2$) by a shear-rate dependent term. Second, given that the binary mixture is in general constituted by particles mechanically different, the reference shear flow states $f_1^{(0)}$ and $f_2^{(0)}$ are completely different. This effect gives rise to terms proportional to $P_{1,ij}^* - (\rho_1/\rho)P_{ij}^*$. Third, in the unthermostatted case, the generalized coefficients are coupled due to the inherent non-Newtonian features of the USF state. Each one of the three effects is a different reflection of the extreme nonequilibrium conditions present in the mixture.

It is apparent that the results presented here in the particular case of Maxwell molecules may be relevant for interpreting computer simulation results. Sarman, Evans, and Baranyai²⁴ carried out time ago molecular dynamics simulations in a strongly sheared Lennard-Jones binary mixture to evaluate the self- and mutual-diffusion tensor by means of Green-Kubo formulae.²⁵ To the best of my knowledge, this is the only computer experiment in which the

shear-rate dependence of the diffusion tensor D_{ij} has been measured. They considered an equimolar Lennard-Jones mixture at two different densities and the parameters in the potential were adjusted to model an argon-krypton mixture, which means that the two components are fairly similar. As already said in Ref. 13, when one considers this type of mixture ($x_1 = 0.5$, $m_1/m_2 = 0.48$, $\kappa_{11} = \kappa_{22} = \kappa_{12}$) in the thermostatted case, the general qualitative dependence of the (reduced) mutual diffusion tensor $D_{ij}(a^*)/D_0$ on the (reduced) shear rate agrees quite well with computer simulations. Thus, theory and simulation predict that in general, the xx element increases to a maximum and then it decreases again, while the yy element decreases with increasing shear rate. The off-diagonal elements xy and yx are negative and their magnitude increases with a^* for not very large values of the shear rate. However, kinetic theory predicts that $|D_{xy}| > |D_{yx}|$, while the opposite happens in computer simulations. On the other hand, at a quantitative level, the influence of shear flow on diffusion is much more modest in the molecular dynamics simulations than the one found theoretically for dilute gases. This is probably due to the fact that the shear rates (in reduced units) applied in the simulations are not large enough to observe significant changes of the diffusion tensor relative to its equilibrium value. An alternative to overcome the difficulties for reaching large shear rates in nonequilibrium molecular dynamics at low-density is the direct simulation Monte Carlo method.²⁶ I hope that the results derived here for Maxwell molecules for D_{ij} , $D_{p,ij}$ and $D_{T,ij}$ stimulate the performance of Monte Carlo simulations to assess the reliability of the Maxwell results to describe mass transport in strongly sheared mixtures for more realistic interaction potentials.

As said before, it must be noted that, in order to observe large effects of shear flow on the tensors $\{D_{ij}, D_{p,ij}, D_{T,ij}\}$, the (reduced) shear rate must be at least of the order of 1. This means that for the inert gas fluids considered in this paper, non-Newtonian effects on mass transport could be observable for shear rates practically unattainable in the laboratory. In this sense, one should look at fluids that are observed to be non-Newtonian, such as colloidal suspensions, polymeric liquids, gels, \dots .^{27,28}

Although the results derived in this paper have been focused on the mass transport, the remaining transport coefficients associated with the pressure tensor $P_{ij}^{(1)}$ and the heat flux vector $\mathbf{q}^{(1)}$ could be determined from the integral equations (3.18)–(3.21). Nevertheless, in practice this calculation cannot be carried out analytically by using the Boltzmann equation since the fourth-degree moments of USF (whose explicit expressions are not known in the Boltzmann equation, except for a single gas⁶) are needed to get the heat flux. In order to overcome such a difficulty one can use a model kinetic equation that preserves the essential features of the true Boltzmann equation but admits a more practical analysis. Perhaps the most well-known model for gas mixtures is the Gross-Krook (GK) kinetic model.²⁹ In this model the Boltzmann operator $J_{rs}[f_r, f_s]$ is replaced by the relaxation term

$$J_{rs}[f_r, f_s] \rightarrow -\nu_{rs}(f_r - f_{rs}), \quad (6.1)$$

where

$$f_{rs} = n_r \left(\frac{m_r}{2\pi k_B T_{rs}} \right)^{3/2} \exp \left[-\frac{m_r}{2k_B T_{rs}} (\mathbf{v} - \mathbf{u}_{rs})^2 \right] \quad (6.2)$$

and

$$\mathbf{u}_{rs} = \frac{m_r \mathbf{u}_r + m_s \mathbf{u}_s}{m_r + m_s}, \quad (6.3)$$

$$T_{rs} = T_r + 2 \frac{m_r m_s}{(m_r + m_s)^2} \left[(T_s - T_r) + \frac{m_s}{6k_B} (\mathbf{u}_r - \mathbf{u}_s)^2 \right]. \quad (6.4)$$

The partial temperatures T_r are defined by Eq. (2.5). For Maxwell molecules, the effective collision frequency ν_{rs} is given by

$$\nu_{rs} = A n_s \left(\kappa_{rs} \frac{m_r + m_s}{m_r m_s} \right)^{1/2}, \quad (6.5)$$

where A is a constant to be fixed by requiring that the model reproduces some transport coefficient of the Boltzmann equation. An exact solution to the GK kinetic model for a binary mixture in USF has been found.³¹ The comparison of the GK results with those from the Boltzmann equation⁴ at the level of the rheological properties shows good agreement, confirming the reliability of the GK model in computing transport properties in far from equilibrium situations as well. Starting from the USF solution of the GK model, the fluxes $P_{ij}^{(1)}$ and $\mathbf{q}^{(1)}$ are obtained in Appendix D in the thermostatted case. With all the transport coefficients known, the constitutive equations for the

mass, momentum and heat fluxes are completed and the corresponding set of closed hydrodynamic equations for the mixture can be derived. This allows one to perform a linear stability analysis of the hydrodynamic equations with respect to the USF and determine the conditions for instabilities at long wavelengths. Previous results for a single gas⁵ have shown that USF is unstable when the perturbations are along the velocity gradient (y direction). The problem now is to extend this analysis to the case of multicomponent systems. Work along this line will be reported in the near future.

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APPENDIX A: CHAPMAN–ENSKOG-LIKE EXPANSION

In this Appendix, some technical details on the determination of the first-order approximation $f_1^{(1)}$ by means of the Chapman–Enskog-like expansion are provided. Inserting the expansions (3.9) and (3.11) into Eq. (3.1a), one gets the kinetic equation for $f_1^{(1)}$:

$$\partial_t^{(0)} f_1^{(1)} - \frac{\partial}{\partial V_i} (a_{ij} V_j + \alpha V_i) f_1^{(1)} + \alpha \delta \mathbf{u} \cdot \frac{\partial f_1^{(1)}}{\partial \mathbf{V}} + \mathcal{L}_1 f_1^{(1)} + \mathcal{M}_1 f_2^{(1)} = - \left[\partial_t^{(1)} + (\mathbf{V} + \mathbf{u}_0) \cdot \nabla \right] f_1^{(1)}. \quad (\text{A1})$$

The velocity dependence on the right-hand side of Eq. (A1) can be obtained from the macroscopic balance equations (3.2)–(3.4) to first order in the gradients. They are given by

$$\partial_t^{(1)} x_1 = -(\mathbf{u}_0 + \delta \mathbf{u}) \cdot \nabla x_1, \quad (\text{A2})$$

$$\partial_t^{(1)} \delta \mathbf{u} = -(\mathbf{u}_0 + \delta \mathbf{u}) \cdot \nabla \delta \mathbf{u} - \rho^{-1} \nabla \cdot \mathbf{P}^{(0)}, \quad (\text{A3})$$

$$\partial_t^{(1)} p = -(\mathbf{u}_0 + \delta \mathbf{u}) \cdot \nabla p - p \nabla \cdot \delta \mathbf{u} - \frac{2}{3} \left(a P_{xy}^{(1)} + \mathbf{P}^{(0)} : \nabla \delta \mathbf{u} \right), \quad (\text{A4})$$

$$\partial_t^{(1)} T = -(\mathbf{u}_0 + \delta \mathbf{u}) \cdot \nabla T - \frac{2}{3n} \left(a P_{xy}^{(1)} + \mathbf{P}^{(0)} : \nabla \delta \mathbf{u} \right), \quad (\text{A5})$$

where use has been made of the result $\mathbf{j}_1^{(0)} = \mathbf{q}^{(0)} = \mathbf{0}$. In addition,

$$P_{ij}^{(1)} = \sum_s m_s \int d\mathbf{c} c_i c_j f_s^{(1)}(\mathbf{c}). \quad (\text{A6})$$

Use of Eqs. (A2)–(A5) in Eq. (A1) yields

$$\begin{aligned} \partial_t^{(0)} f_1^{(1)} - \frac{\partial}{\partial V_i} (a_{ij} V_j + \alpha V_i) f_1^{(1)} + \alpha \delta \mathbf{u} \cdot \frac{\partial f_1^{(1)}}{\partial \mathbf{V}} + \mathcal{L}_1 f_1^{(1)} + \mathcal{M}_1 f_2^{(1)} = & \mathbf{A}_1 \cdot \nabla x_1 \\ & + \mathbf{B}_1 \cdot \nabla p + \mathbf{C}_1 \cdot \nabla T + \mathbf{D}_1 : \nabla \delta \mathbf{u}, \end{aligned} \quad (\text{A7})$$

where

$$A_{1,i}(\mathbf{c}) = -\frac{\partial f_1^{(0)}}{\partial x_1} c_i + \frac{1}{\rho} \frac{\partial f_1^{(0)}}{\partial \delta u_j} \frac{\partial P_{ij}^{(0)}}{\partial x_1}, \quad (\text{A8})$$

$$B_{1,i}(\mathbf{c}) = -\frac{\partial f_1^{(0)}}{\partial p} c_i + \frac{1}{\rho} \frac{\partial f_1^{(0)}}{\partial \delta u_j} \frac{\partial P_{ij}^{(0)}}{\partial p}, \quad (\text{A9})$$

$$C_{1,i}(\mathbf{c}) = -\frac{\partial f_1^{(0)}}{\partial T} c_i + \frac{1}{\rho} \frac{\partial f_1^{(0)}}{\partial \delta u_j} \frac{\partial P_{ij}^{(0)}}{\partial T}, \quad (\text{A10})$$

$$D_{1,ij}(\mathbf{c}) = p \frac{\partial f_1^{(0)}}{\partial p} \delta_{ij} - \frac{\partial f_1^{(0)}}{\partial \delta u_i} c_j + \frac{2}{3p} \left(P_{ij}^{(0)} - a \eta_{xyij} \right) \left(p \frac{\partial}{\partial p} + T \frac{\partial}{\partial T} \right) f_1^{(0)}. \quad (\text{A11})$$

Upon writing Eq. (A11) use has been made of the expression of the total pressure tensor $P_{ij}^{(1)}$ of the mixture^{5,6}

$$P_{ij}^{(1)} = -\eta_{ijk\ell} \frac{\partial \delta u_k}{\partial r_\ell}, \quad (\text{A12})$$

where $\eta_{ijk\ell}$ is the viscosity tensor.

The solution to Eq. (A7) has the form given by Eq. (3.17), where the coefficients \mathcal{A}_1 , \mathcal{B}_1 , \mathcal{C}_1 , and \mathcal{D}_1 are functions of the peculiar velocity and the hydrodynamic fields x_1 , p , T , and $\delta \mathbf{u}$. The time derivative acting on these quantities can be evaluated with the replacement

$$\partial_t^{(0)} \rightarrow -\left(\frac{2}{3p} a P_{xy}^{(0)} + 2\alpha \right) (p \partial_p + T \partial_T). \quad (\text{A13})$$

Moreover, there are contributions from $\partial_t^{(0)}$ acting on the pressure, temperature, and velocity gradients given by

$$\begin{aligned} \partial_t^{(0)} \nabla p &= -\nabla \left(\frac{2}{3} a P_{xy}^{(0)} + 2p\alpha \right) \\ &= -\left(\frac{2a}{3} \frac{\partial P_{xy}^{(0)}}{\partial x_1} + 2p \frac{\partial \alpha}{\partial x_1} \right) \nabla x_1 - \left(\frac{2a}{3} \frac{\partial P_{xy}^{(0)}}{\partial p} + 2\alpha + 2 \frac{\partial \alpha}{\partial p} \right) \nabla p \\ &\quad - \left(\frac{2a}{3} \frac{\partial P_{xy}^{(0)}}{\partial T} + 2p \frac{\partial \alpha}{\partial T} \right) \nabla T, \end{aligned} \quad (\text{A14})$$

$$\begin{aligned} \partial_t^{(0)} \nabla T &= -\nabla \left(\frac{2T}{3p} a P_{xy}^{(0)} + 2T\alpha \right) \\ &= -\left(\frac{2aT}{3p} \frac{\partial P_{xy}^{(0)}}{\partial x_1} + 2T \frac{\partial \alpha}{\partial x_1} \right) \nabla x_1 + \left(\frac{2aT}{3p^2} P_{xy}^{(0)} - \frac{2aT}{3p} \frac{\partial P_{xy}^{(0)}}{\partial p} - 2T \frac{\partial \alpha}{\partial p} \right) \nabla p \\ &\quad - \left(\frac{2a}{3p} P_{xy}^{(0)} + \frac{2aT}{3p} \frac{\partial P_{xy}^{(0)}}{\partial T} + 2\alpha + 2T \frac{\partial \alpha}{\partial T} \right) \nabla T, \end{aligned} \quad (\text{A15})$$

$$\partial_t^{(0)} \nabla_i \delta u_j = \nabla_i \partial_t^{(0)} \delta u_j = -a_{jk} \nabla_i \delta u_k. \quad (\text{A16})$$

The corresponding integral equations (3.18)–(3.20) can be obtained when one identifies coefficients of independent gradients in Eq. (A7) and takes into account Eqs. (A14)–(A16) and the mathematical property

$$\begin{aligned} \partial_t^{(0)} X &= \frac{\partial X}{\partial p} \partial_t^{(0)} p + \frac{\partial X}{\partial T} \partial_t^{(0)} T + \frac{\partial X}{\partial \delta u_i} \partial_t^{(0)} \delta u_i \\ &= -\left(\frac{2}{3p} a P_{xy}^{(0)} + 2\alpha \right) \left(p \frac{\partial}{\partial p} + T \frac{\partial}{\partial T} \right) X + a_{ij} \delta u_j \frac{\partial X}{\partial c_i}, \end{aligned} \quad (\text{A17})$$

where in the last step it has been taken into account that X depends on $\delta \mathbf{u}$ through $\mathbf{c} = \mathbf{V} - \delta \mathbf{u}$.

APPENDIX B: GENERALIZED TRANSPORT COEFFICIENTS ASSOCIATED WITH THE MASS TRANSPORT

In the unthermostatted case ($\alpha = 0$), the integral equations defining the generalized transport coefficients D_{ij} , $D_{p,ij}$ and $D_{T,ij}$ are given by Eqs. (4.1)–(4.3). To get these coefficients, one multiplies (4.1)–(4.3) by $m_1 c_i$ and integrates

over velocity. The result is

$$\begin{aligned} & \frac{2}{3p} a P_{xy}^{(0)} (p\partial_p + T\partial_T) \left(\frac{m_1 m_2 n}{\rho} D_{ij} \right) - \frac{m_1 m_2 n}{\rho} \left(a_{ik} D_{kj} + \frac{\rho \lambda_{12}}{m_1 m_2} D_{ij} \right) \\ &= m_1 \int d\mathbf{c} \, c_i A_{1,j} - \frac{2a\rho}{3p} (\partial_{x_1} P_{xy}^{(0)}) (D_{p,ij} + D_{T,ij}), \end{aligned} \quad (\text{B1})$$

$$\begin{aligned} & \frac{2}{3p} a P_{xy}^{(0)} (p\partial_p + T\partial_T) \left(\frac{\rho}{p} D_{p,ij} \right) - \frac{\rho}{p} \left[a_{ik} D_{p,kj} + \left(\frac{\rho \lambda_{12}}{m_1 m_2} - \frac{2a}{3p} \partial_p P_{xy}^{(0)} \right) D_{p,ij} \right] \\ &= m_1 \int d\mathbf{c} \, c_i B_{1,j} + \frac{2a\rho}{3p^2} D_{T,ij} (1 - p\partial_p) P_{xy}^{(0)}, \end{aligned} \quad (\text{B2})$$

$$\begin{aligned} & \frac{2}{3p} a P_{xy}^{(0)} (p\partial_p + T\partial_T) \left(\frac{\rho}{T} D_{T,ij} \right) - \frac{\rho}{T} \left[a_{ik} D_{T,kj} + \left(\frac{\rho \lambda_{12}}{m_1 m_2} - \frac{2a}{3p} (1 + T\partial_T) P_{xy}^{(0)} \right) D_{T,ij} \right] \\ &= m_1 \int d\mathbf{c} \, c_i C_{1,j} - \frac{2a\rho}{3p} D_{p,ij} (\partial_T P_{xy}^{(0)}), \end{aligned} \quad (\text{B3})$$

where

$$P_{s,ij}^{(0)} = m_s \int d\mathbf{c} \, c_i c_j f_s^{(0)}. \quad (\text{B4})$$

Upon writing Eqs. (B1)–(B3), use has been made of the relation (2.12), which yields the results

$$m_1 \int d\mathbf{c} \, c_i (\mathcal{L}_1 \mathbf{A}_1 + \mathcal{M}_1 \mathbf{A}_2) = -n \lambda_{12} D_{ij}, \quad (\text{B5a})$$

$$m_1 \int d\mathbf{c} \, c_i (\mathcal{L}_1 \mathbf{B}_1 + \mathcal{M}_1 \mathbf{B}_2) = -\frac{\rho^2 \lambda_{12}}{m_1 m_2 p} D_{p,ij}, \quad (\text{B5b})$$

$$m_1 \int d\mathbf{c} \, c_i (\mathcal{L}_1 \mathbf{C}_1 + \mathcal{M}_1 \mathbf{C}_2) = -\frac{\rho^2 \lambda_{12}}{m_1 m_2 T} D_{T,ij}. \quad (\text{B5c})$$

The velocity integrals appearing in Eqs. (B1)–(B3) can be performed by using Eqs. (A8)–(A10),

$$m_1 \int d\mathbf{c} \, c_i A_{1,j} = - \left(\partial_{x_1} P_{1,ij}^{(0)} - \frac{\rho_1}{\rho} \partial_{x_1} P_{ij}^{(0)} \right), \quad (\text{B6})$$

$$m_1 \int d\mathbf{c} \, c_i B_{1,j} = -\partial_p \left(P_{1,ij}^{(0)} - \frac{\rho_1}{\rho} P_{ij}^{(0)} \right), \quad (\text{B7})$$

$$m_1 \int d\mathbf{c} \, c_i C_{1,j} = -\partial_T \left(P_{1,ij}^{(0)} - \frac{\rho_1}{\rho} P_{ij}^{(0)} \right). \quad (\text{B8})$$

The generalized transport coefficients D_{ij} , $D_{p,ij}$, and $D_{T,ij}$ can be written as $D_{ij} = D_0 D_{ij}^*(a^*)$, $D_{p,ij} = D_{p,0} D_{p,ij}^*(a^*)$, and $D_{T,ij} = D_{T,0} D_{T,ij}^*(a^*)$ where D_{ij}^* , $D_{p,ij}^*$, and $D_{T,ij}^*$ are dimensionless functions of the shear rate. Moreover, from dimensional analysis, $D_0 \sim T$, $D_{p,0} \sim T^2/p$, and $D_{T,0} \sim T^2/p$. Therefore,

$$(p\partial_p + T\partial_T) \left(\frac{m_1 m_2 n}{\rho} D_{ij} \right) = (p\partial_p + T\partial_T) \left(\frac{m_1 m_2 n}{\rho} D_0 D_{ij}^* \right) = \frac{m_1 m_2 n}{\rho} D_{ij}, \quad (\text{B9})$$

$$(p\partial_p + T\partial_T) \left(\frac{\rho}{p} D_{p,ij} \right) = (p\partial_p + T\partial_T) \left(\frac{\rho}{p} D_{p,0} D_{p,ij}^* \right) = 0, \quad (\text{B10})$$

$$(p\partial_p + T\partial_T) \left(\frac{\rho}{T} D_{T,ij} \right) = (p\partial_p + T\partial_T) \left(\frac{\rho}{T} D_{T,0} D_{T,ij}^* \right) = 0, \quad (\text{B11})$$

where use has been made of the identity

$$(p\partial_p + T\partial_T) X(a^*) = (\partial_{a^*} X) (p\partial_p a^* + T\partial_T a^*) = 0, \quad (\text{B12})$$

with $a^* = a/\zeta \sim T/p$. Taking into account the above results one arrives at the set of algebraic equations (4.7)–(4.9).

APPENDIX C: RHEOLOGICAL PROPERTIES IN THE TRACER LIMIT

The explicit expressions for the pressure tensors $P_{s,ij}^* \equiv P_{s,ij}/p$ in the USF are provided in this Appendix for the special case of tracer limit ($x_1 \rightarrow 0$). The nonzero elements of $P_{2,ij}^*$ are given by¹⁰

$$P_{2,yy}^* = P_{2,zz}^* = \frac{1}{1 + 2\omega\alpha^*}, \quad (C1)$$

$$P_{2,xx}^* = \frac{1 + 6\omega\alpha^*}{1 + 2\omega\alpha^*}, \quad (C2)$$

$$P_{2,xy}^* = -3\frac{\alpha^*}{a^*} = -\frac{\omega a^*}{(1 + 2\omega\alpha^*)^2}, \quad (C3)$$

where $a^* = a/\zeta$, $\alpha^* = \alpha/\zeta$, ζ being defined by Eq. (4.4). Moreover,

$$\omega = \frac{2}{\gamma_{22}(1 + \mu)}, \quad \gamma_{22} = \sqrt{\frac{\kappa_{22}}{\kappa_{12}} \frac{1 + \mu}{\mu}}, \quad (C4)$$

where $\mu = m_1/m_2$ is the mass ratio. The (reduced) thermostat parameter is given by $\alpha^* = \max(\alpha_0, \alpha'_0)$ where^{4,30}

$$\alpha_0 = \frac{1}{2\omega}G(\omega a^*), \quad \alpha'_0 = \frac{1}{4\mu}G(2\mu a^*) - \frac{1}{2}\gamma_{12}, \quad (C5)$$

where $G(z) = \frac{4}{3}\sinh^2[\frac{1}{6}\cosh^{-1}(1 + 9z^2)]$ and $\gamma_{12} = \lambda_{12}/\lambda'_{12} = 0.648$. Usually, $\alpha_0 > \alpha'_0$ except for very large shear rates and/or very disparate mass binary mixtures.³⁰

The nonzero elements of $P_{1,ij}^*$ are given by¹⁰

$$P_{1,yy}^* = P_{1,zz}^* = \frac{x_1}{\Delta(1 + 2\omega\alpha^*)} \left\{ (\gamma_{12} - \frac{1}{2})(2\alpha^* + \epsilon)^2 + (2\gamma_{12} - 1)\alpha^*\beta(1 + \omega\epsilon + 4\omega\alpha^*) \right. \\ \left. + \frac{1}{2}(1 + 2\omega\alpha^*)(2\alpha^* + \epsilon)^2 \right\}, \quad (C6)$$

$$P_{1,xx}^* = \frac{x_1}{\Delta(1 + 2\omega\alpha^*)} \left\{ (\gamma_{12} - \frac{1}{2})(2\alpha^* + \epsilon)^2 + 3(2\gamma_{12} - 1)\alpha^*(1 + \omega\epsilon + 4\omega\alpha^*) \left(2\alpha^* + \epsilon - \frac{2}{3}\beta \right) \right. \\ \left. + \frac{1}{2}(1 + 2\omega\alpha^*)[(2\alpha^* + \epsilon)^2 + 2a^{*2}] + (2\gamma_{12} - 1)a^{*2} \right\}, \quad (C7)$$

$$P_{1,xy}^* = -\frac{x_1\omega a^*}{\Delta(1 + 2\omega\alpha^*)^2} \left\{ (\gamma_{12} - \frac{1}{2})(2\alpha^* + \gamma_{12})(2\alpha^* + \epsilon) + (\gamma_{12} - \frac{1}{2})\frac{1 + 2\omega\alpha^*}{\omega} \right. \\ \left. \times (2\alpha^* + \epsilon + 2\omega\alpha^*\beta) + \frac{1}{2\omega}(1 + 2\omega\alpha^*)^2(2\alpha^* + \epsilon) \right\}, \quad (C8)$$

where $\epsilon = \gamma_{12} + \beta$, $\beta = 1/2\mu$, and

$$\Delta = (2\alpha^* + \epsilon)^2(2\alpha^* + \gamma_{12}) - \frac{2}{3}\beta a^{*2}. \quad (C9)$$

APPENDIX D: MOMENTUM AND HEAT TRANSPORT AROUND USF FROM THE GK MODEL

This Appendix addresses the evaluation of the fluxes $P_{ij}^{(1)}$ and $\mathbf{q}^{(1)}$ in the thermostatted case from the GK kinetic model (6.1). The first order corrections to the fluxes are

$$P_{ij}^{(1)} = -\sum_s \eta_{s,ijkl} \frac{\partial \delta u_k}{\partial r_\ell}, \quad (D1)$$

$$q_i^{(1)} = - \sum_s D''_{s,ij} \frac{\partial x_1}{\partial r_j} - \sum_s L_{s,ij} \frac{\partial p}{\partial r_j} - \sum_s \lambda_{s,ij} \frac{\partial T}{\partial r_j}, \quad (\text{D2})$$

where the partial contributions to the transport coefficients are defined as

$$\eta_{s,ijkl} = -m_s \int d\mathbf{c} c_i c_j \mathcal{D}_{s,kl}(\mathbf{c}), \quad (\text{D3})$$

$$D''_{s,ij} = -\frac{m_s}{2} \int d\mathbf{c} c^2 c_i \mathcal{A}_{s,j}(\mathbf{c}), \quad (\text{D4})$$

$$L_{s,ij} = -\frac{m_s}{2} \int d\mathbf{c} c^2 c_i \mathcal{B}_{s,j}(\mathbf{c}), \quad (\text{D5})$$

$$\lambda_{s,ij} = -\frac{m_s}{2} \int d\mathbf{c} c^2 c_i \mathcal{C}_{s,j}(\mathbf{c}). \quad (\text{D6})$$

From the above partial contributions one can get the generalized shear viscosity $\eta_{ijkl} = \eta_{1,ijkl} + \eta_{2,ijkl}$, the generalized Duffour coefficient $D''_{ij} = D''_{1,ij} + D''_{2,ij}$, the generalized pressure energy coefficient $L_{ij} = L_{1,ij} + L_{2,ij}$, and the generalized thermal conductivity $\lambda_{ij} = \lambda_{1,ij} + \lambda_{2,ij}$. The quantities $\{\mathcal{A}_{s,i}, \mathcal{B}_{s,i}, \mathcal{C}_{s,i}, \mathcal{D}_{s,ij}\}$ still verify the integral equations (3.18)–(3.21) (with $\alpha = -aP_{xy}^{(0)}/3p$) with the only replacement

$$\mathcal{L}_1 f_1^{(1)} + \mathcal{M}_1 f_2^{(1)} \rightarrow \nu_1 f_1^{(1)} - \nu_{11} f_{11}^{(1)} - \nu_{12} f_{12}^{(1)}, \quad (\text{D7})$$

where $\nu_1 = \nu_{11} + \nu_{12}$,

$$f_{11}^{(1)} = \frac{f_{11}^{(0)}}{n_1 k_B T_1} \mathbf{c} \cdot \mathbf{j}_1^{(1)}, \quad f_{12}^{(1)} = \frac{f_{12}^{(0)}}{n_1 n_2 k_B T_{12}} \mu_{12} (n_2 - n_1) \mathbf{c} \cdot \mathbf{j}_1^{(1)}, \quad (\text{D8})$$

and

$$f_{rs}^{(0)} = n_r \left(\frac{m_r}{2\pi k_B T_{rs}} \right)^{3/2} \exp \left(-\frac{m_r c^2}{2k_B T_{rs}} \right). \quad (\text{D9})$$

In Eq. (D8), $\mu_{rs} = m_r/(m_r + m_s)$.

In order to get the coefficients $\eta_{s,ijkl}$, $D''_{s,ij}$, $L_{s,ij}$ and $\lambda_{s,ij}$, it is convenient to introduce the velocity moments

$$X_{k,\ell,m}^{(i)} = \int d\mathbf{c} c_x^k c_y^\ell c_z^m \mathcal{A}_{1,i}, \quad (\text{D10})$$

$$Y_{k,\ell,m}^{(i)} = \int d\mathbf{c} c_x^k c_y^\ell c_z^m \mathcal{B}_{1,i}, \quad (\text{D11})$$

$$Z_{k,\ell,m}^{(i)} = \int d\mathbf{c} c_x^k c_y^\ell c_z^m \mathcal{C}_{1,i}, \quad (\text{D12})$$

$$W_{k,\ell,m}^{(ij)} = \int d\mathbf{c} c_x^k c_y^\ell c_z^m \mathcal{D}_{1,ij}, \quad (\text{D13})$$

and similar definitions for the species 2. The knowledge of the above moments allows one to get the expressions of the coefficients $\eta_{1,ijkl}$, $D''_{1,ij}$, $L_{1,ij}$ and $\lambda_{1,ij}$. The method to evaluate the moments $X_{k,\ell,m}^{(i)}$, $Y_{k,\ell,m}^{(i)}$, $Z_{k,\ell,m}^{(i)}$ and $W_{k,\ell,m}^{(ij)}$ is quite similar. Here, as an example, the mathematical steps to determine the moments $X_{k,\ell,m}^{(i)}$ associated with the transport coefficients $D''_{1,ij}$ will be analyzed in detail. First, in the thermostated case, Eq. (3.18) with the change (D7) becomes

$$- \left(a c_y \frac{\partial}{\partial c_x} - \nu_1 + \alpha \frac{\partial}{\partial \mathbf{c}} \cdot \mathbf{c} \right) \mathcal{A}_{1,i} + \frac{m_1 m_2 n}{\rho} \left(\frac{\nu_{11}}{n_1 k_B T_1} f_{11}^{(0)} + \frac{\nu_{12}}{n_1 n_2 k_B T_{12}} \mu_{12} (n_2 - n_1) f_{12}^{(0)} \right) c_j D_{ji} = A_{1,i}, \quad (\text{D14})$$

where \mathbf{A}_1 is given by Eq. (A8). Upon writing (D14) use has been made of the constitutive form (3.24) for the mass flux. Now, we multiply Eq. (D14) by $c_x^k c_y^\ell c_z^m$ and integrate over velocity. After some algebra, we get

$$akX_{k-1,\ell+1,m}^{(i)} + [\nu_1 + (k + \ell + m)\alpha] X_{k,\ell,m}^{(i)} = R_{k,\ell,m}^{(i)}, \quad (\text{D15})$$

where

$$R_{k,\ell,m}^{(i)} = \bar{A}_{1,i} - \frac{m_1 m_2 n}{\rho} \left(\frac{2k_B T}{m_1} \right)^{(k+\ell+m+1)/2} \left[\frac{\nu_{11}}{k_B T} \chi_1^{(k+\ell+m-1)/2} + \frac{\nu_{12}}{n_2 k_B T} \mu_{12} (n_2 - n_1) \chi_{12}^{(k+\ell+m-1)/2} \right] \\ \times \Lambda_{k+\delta_{jx}, \ell+\delta_{jy}, m+\delta_{jz}} D_{ji}, \quad (\text{D16})$$

$$\bar{A}_{1,i} \equiv \int d\mathbf{c} c_x^k c_y^\ell c_z^m A_{1,i} = -\frac{\partial}{\partial x_1} M_{k+\delta_{ix}, \ell+\delta_{iy}, m+\delta_{iz}} \\ + \frac{1}{\rho} \frac{\partial P_{ij}^{(0)}}{\partial x_1} (\delta_{jx} k M_{k-1,\ell,m} + \delta_{jy} \ell M_{k,\ell-1,m} + \delta_{jz} m M_{k,\ell,m-1}). \quad (\text{D17})$$

In Eqs. (D16) and (D17), we have introduced the temperature ratios $\chi_1 = T_1/T$ and $\chi_{12} = T_{12}/T$ and the (unperturbed) moments of the USF

$$M_{k,\ell,m} = \int d\mathbf{c} c_x^k c_y^\ell c_z^m f_1^{(0)}(\mathbf{c}). \quad (\text{D18})$$

The explicit shear-rate dependence of χ_1 , χ_{12} and $M_{k,\ell,m}$ can be found in Ref. 31. Moreover,

$$\Lambda_{k,\ell,m} = \pi^{-3/2} \Gamma\left(\frac{k+1}{2}\right) \Gamma\left(\frac{\ell+1}{2}\right) \Gamma\left(\frac{m+1}{2}\right) \quad (\text{D19})$$

if (k, ℓ, m) are even, being zero otherwise. The solution to Eq. (D15) can be written as

$$X_{k,\ell,m}^{(i)} = \sum_{q=0}^k \frac{k!}{(k-q)!} (-a)^q [\nu_1 + (k + \ell + m)\alpha]^{-(1+q)} R_{k-q,\ell+q,m}^{(i)}. \quad (\text{D20})$$

Note that Eq. (D20) is still formal since one needs to know the coefficients D_{ij} . They can be consistently determined from their definitions (3.25). Once these coefficients are known, Eq. (D20) allows one to get the coefficients $D_{1,ij}''$.

The same method can be applied to evaluate the remaining moments. The moments $Y_{k,\ell,m}^{(i)}$ and $Z_{k,\ell,m}^{(i)}$ are given by

$$Y_{k,\ell,m}^{(i)} = \sum_{q=0}^k \frac{k!}{(k-q)!} (-a)^q [\nu_1 + (k + \ell + m)\alpha]^{-(1+q)} S_{k-q,\ell+q,m}^{(i)}, \quad (\text{D21})$$

$$Z_{k,\ell,m}^{(i)} = \sum_{q=0}^k \frac{k!}{(k-q)!} (-a)^q [\nu_1 + (k + \ell + m)\alpha]^{-(1+q)} T_{k-q,\ell+q,m}^{(i)}, \quad (\text{D22})$$

where

$$S_{k,\ell,m}^{(i)} = \bar{B}_{1,i} - \frac{\rho}{p} \left(\frac{2k_B T}{m_1} \right)^{(k+\ell+m+1)/2} \left[\frac{\nu_{11}}{k_B T} \chi_1^{(k+\ell+m-1)/2} + \frac{\nu_{12}}{n_2 k_B T} \mu_{12} (n_2 - n_1) \chi_{12}^{(k+\ell+m-1)/2} \right] \\ \times \Lambda_{k+\delta_{jx}, \ell+\delta_{jy}, m+\delta_{jz}} D_{p,ji}, \quad (\text{D23})$$

$$T_{k,\ell,m}^{(i)} = \bar{C}_{1,i} - \frac{\rho}{T} \left(\frac{2k_B T}{m_1} \right)^{(k+\ell+m+1)/2} \left[\frac{\nu_{11}}{k_B T} \chi_1^{(k+\ell+m-1)/2} + \frac{\nu_{12}}{n_2 k_B T} \mu_{12} (n_2 - n_1) \chi_{12}^{(k+\ell+m-1)/2} \right] \\ \times \Lambda_{k+\delta_{jx}, \ell+\delta_{jy}, m+\delta_{jz}} D_{T,ji}. \quad (\text{D24})$$

The expressions of $\bar{B}_{1,i}$ and $\bar{C}_{1,i}$ are formally identical to that of $\bar{A}_{1,i}$, except that the operator ∂_{x_1} appearing in (D17) must be replaced by the operators ∂_p and ∂_T in the cases of $\bar{B}_{1,i}$ and $\bar{C}_{1,i}$, respectively. Finally, the expression of $W_{k,\ell,m}^{(ij)}$ is

$$W_{k,\ell,m}^{(ij)} = \sum_{q=0}^k \frac{k!}{(k-q)!} (-a)^q [\nu_1 + (k + \ell + m)\alpha]^{-(1+q)} \left[U_{k-q,\ell+q,m}^{(ij)} + a\delta_{iy} W_{k,\ell,m}^{(xj)} \right], \quad (D25)$$

where

$$\begin{aligned} U_{k,\ell,m}^{(ij)} = & -\delta_{ij} \left(1 - p \frac{\partial}{\partial p} \right) M_{k,\ell,m} + \frac{2}{3p} \left(P_{ij}^{(0)} - a\eta_{xyij} \right) \left(p \frac{\partial}{\partial p} + T \frac{\partial}{\partial T} \right) M_{k,\ell,m} \\ & - M_{k,\ell,m} (\delta_{ix}\delta_{jx}k + \delta_{iy}\delta_{jy}\ell + \delta_{iz}\delta_{jz}m) \\ & - k\delta_{ix} (\delta_{jy}M_{k-1,\ell+1,m} + \delta_{jz}M_{k-1,\ell,m+1}) \\ & - \ell\delta_{iy} (\delta_{jx}M_{k+1,\ell-1,m} + \delta_{jz}M_{k,\ell-1,m+1}) \\ & - m\delta_{iz} (\delta_{jx}M_{k+1,\ell,m-1} + \delta_{jy}M_{k,\ell+1,m-1}). \end{aligned} \quad (D26)$$

The transport coefficients $D_{1,ij}''$, $L_{1,ij}$, $\lambda_{1,ij}$, and $\eta_{1,ijkl}$ can be obtained from Eqs. (D20), (D21), (D22) and (D25), respectively, in terms of the shear rate and the parameters of the mixture. Their respective counterparts for species 2 can be easily determined from them by making the changes: $m_1 \rightarrow m_2$, $n_1 \rightarrow n_2$, and $\kappa_{11} \rightarrow \kappa_{22}$. The expression of the Duffour tensor D_{ij}'' coincides with the one obtained before¹⁴ in a stationary state with $\nabla p = \nabla T = 0$. Finally, note that the USF moments $M_{k,\ell,m}$ can be written as³¹

$$M_{k,\ell,m} = n_1 \left(\frac{2k_B T}{m_1} \right)^{(k+\ell+m)/2} M_{k,\ell,m}^*, \quad (D27)$$

where the dimensionless moments $M_{k,\ell,m}^*$ depend on p and T through their dependence on a^* . Consequently,

$$p\partial_p M_{k,\ell,m} = n_1 \left(\frac{2k_B T}{m_1} \right)^{(k+\ell+m)/2} (1 - a^* \partial_{a^*}) M_{k,\ell,m}^*, \quad (D28)$$

$$T\partial_T M_{k,\ell,m} = n_1 \left(\frac{2k_B T}{m_1} \right)^{(k+\ell+m)/2} \left(\frac{k + \ell + m - 2}{2} + a^* \partial_{a^*} \right) M_{k,\ell,m}^*. \quad (D29)$$

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